Experimental evaluation of the detection methods of thermal ionization mass spectrometry for isotopic analysis of ultra-trace level uranium

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ABSTRACT

Thermal ionization mass spectrometry (TIMS)-based isotopic analysis of various amounts of uranium was performed to experimentally evaluate three detection methods: multi-dynamic, dynamic, and static. The analytical performances of the detection methods in terms of accuracy, precision, and measurement uncertainty were not significantly different for the analysis of 1 ng and 100 pg of uranium, whereas using ion counters for detecting $^{238}U^+$ signal intensity slightly enhanced the performance for analyzing 30 pg of uranium. The static detection method improves the analysis performance for 5 pg and 1 pg of uranium due to the higher detection sensitivity of ion counters than faraday cups, elimination of ion signal drift, and increased number of valid data sets in a measurement. The experimental evaluation of the detection methods provides a basis for optimizing the detector configuration of TIMS in terms of the amount of uranium in samples. The uranium isotope ratios in microparticles measured by the static method agreed well with the certified values; this verified the applicability of the static detection method to particle analysis of environmental samples required for nuclear safeguards.

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1. Introduction

Monitoring undeclared nuclear activities for nuclear safeguards and tracking the sample origin for nuclear forensics require highly reliable uranium isotopic analysis [1–4]. Thermal ionization mass spectrometry (TIMS) is one of the most accurate and precise techniques for isotopic analysis, with high instrumental sensitivity and negligible mass discrimination, matrix effect, and spectral interference [5–7]. The aforementioned advantages enable most laboratories in the Network of Analytical Laboratories (NWAL) to adopt TIMS for environmental sample analysis [1].

The amount of uranium contained in environmental samples is mostly at ultra-trace levels. Bulk analysis for determination of the total amount and averaged isotopic ratios of uranium content in a sample is applicable for few or few tens of nanograms of uranium [1,8–10]. On the other hand, particle analysis to determine the isotope ratios of uranium in individual particles deals with much less amounts at the level of a few picograms [1,6,11–15]. Unlike normal analysis of considerable amounts (micro- or milligram levels) of uranium, such as in nuclear

fuel or nuclear waste samples, TIMS measurement of such ultra-trace amounts of uranium requires special techniques to maintain analytical reliability. TIMS-based techniques include filament pretreatment by carburization to enhance sensitivity [16,17], continuous heating of sample filament for modified total evaporation [18], and peak tail correction by statistical approach [19–21]. Similarly, the ion signal collection method must be specialized for the analysis of ultra-trace amounts of uranium.

Accurate determination of uranium isotope ratios requires not only measurement of the major isotopes, ^{238}U and ^{235}U, but also accurate measurement of the minor isotopes, ^{234}U and ^{236}U, the relative amounts of which are less than that of ^{238}U by factors of thousands. For analysis of most environmental samples, even ^{235}U is at sub-picogram levels [1]. Therefore, the ion signals from ^{234}U, ^{235}U, and ^{236}U must be collected by ion counters, and not by faraday cups due to their insufficient detection sensitivity. This implies that the detector configuration for ion signals from uranium isotopes is important for reliable analysis.

The isotopic ratios of uranium ($n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$, $n(^{236}U)/n(^{238}U)$) are measured using three detection methods: dynamic, multi-dynamic, and static. In the dynamic method, one ion counter (IC) is utilized to detect the ion signals of $^{234}U^+$, $^{235}U^+$, $^{236}U^+$, and $^{238}U^+$ by changing the magnetic field consecutively. The dynamic method has the simplest detector configuration, which requires no calibration among multiple detectors. On the other hand, ion signal drift can occur because the detection moment of each isotope is different, resulting in distortion of isotope ratios. Furthermore, relatively large

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amount of sample is required because the ion signal from only one isotope can be collected at a time, while other isotopes are consumed without detection. This is problematic when only ultra-trace amounts of sample are available. In addition, the analysis is impossible when the $^{238}U^+$ ion intensity is above the working range of IC.

In the multi-dynamic method, combinations of an IC and a faraday cup (FAR) are used to detect one of the ion signals of low-abundance isotopes ($^{234}U^+$, $^{235}U^+$, or $^{236}U^+$) along with simultaneous detection of $^{238}U^+$. After a combination of simultaneous detection ($^{234}U^+$ with $^{238}U^+$, $^{235}U^+$ with $^{238}U^+$, or $^{236}U^+$ with $^{238}U^+$) has been achieved for a certain integration time, another detection combination is performed by changing the magnetic field consecutively. Although ion signal drift also occurs in the multi-dynamic mode, chances of distortion in isotope ratios is eliminated because two ion signals are detected simultaneously to produce an isotope ratio. However, relatively large sample amounts are still required, and applicability of the analysis is limited when the $^{238}U^+$ ion intensity is below the working range of faraday cups. Detector calibration is also required between IC and faraday cup.

Multiple detectors (ion counters and faraday cups) are utilized in the static detection method, which enables us to measure all uranium isotopes simultaneously. There are no distortions in isotope ratios due to ion signal drift and no sample wastage. However, special care must be taken in detector calibration among multiple detectors, otherwise the resulting isotope ratios are inconvincible.

Each detection method offers different analytical performances in obtaining uranium isotope ratios. Furthermore, the performances are expected to strongly depend on the amount of uranium. To obtain reliable analytical results, the detector configuration of TIMS must be optimized prior to analysis based on the analytical performance of the detection methods in terms of the uranium amounts of samples. However, to the best of our knowledge, no study on evaluating the analytical performance of the detection methods of TIMS has yet been reported.

In this study, the analytical performance of the three TIMS-based detection methods was experimentally evaluated for isotopic analysis of uranium at ultra-trace levels, in terms of analytical accuracy, precision, and measurement uncertainty. Various amounts of uranium, ranging from nanogram to picogram levels, were tested to evaluate the dependence of analytical performance of the detection methods on sample amounts. Finally, the optimized detection mode for ultra-trace-level uranium analysis was applied for isotopic analysis of individual uranium particles. This study provides a basis for the criteria required to optimize the detector configuration of TIMS in terms of the amount of uranium in samples.

2. Experimental

Nitric acid solutions of a certified reference material (U030, National Bureau of Standards, USA) of different concentrations (approximately 1 μg/g, 100 ng/g, 30 ng/g, 5 ng/g, and 1 ng/g) were used as the uranium samples. 1-μL aliquots of each of the solutions were transferred to background minimized zone-refined rhenium filaments to load approximately 1 ng, 100 pg, 30 pg, 5 pg, and 1 pg of uranium, and then dried with a current of 0.6 A and fixed at 1.8 A for 30 s. Ten replicates for each concentration of uranium sample were prepared and loaded in TIMS for isotopic measurements.

Individual particles from U030 powder and a sample for NUSIMEP-7 (the 7th Nuclear Signatures Interlaboratory Measurement Evaluation Programme) were transferred to TIMS filaments using a microprobe on a three-axis micromanipulator system (MM3M-EM, Kleindiek Nanotechnik, Germany) equipped with a scanning electron microscope (JSM-6610LV, Jeol, Japan) (Fig. 1). Five individual particles of U030 powder (numbered P1–P5) and seven individual particles of NUSIMEP-7 (numbered NU7-1–NU7-7) were prepared using this procedure. The particle sizes for U030 and NUSIMEP-7 were ~1 μm and ~0.8 μm in diameter, respectively. The certified values of U030 and the sample for NUSIMEP-7 are listed in Table 1. The NUSIMEP-7 sample contained

two types of particles (Depositions 1 and 2) with different uranium isotope ratios [22,23].

The experimental setup for isotope measurements using TIMS (TRITON Plus, Thermo Fisher Scientific, Germany) with the continuous heating method has been described in detail elsewhere [10,15,20,24]. Three types of detector were adopted: secondary electron multiplier (SEM), compact discrete dynode (CDD), and faraday cup (FAR). The first two types are classified as ion counters, which transduces the ion signal intensity into count (in cps), and the difference is their sizes. Tables 2, 3, and 4 show the detector configurations in the multi-dynamic, dynamic, and static detection methods, respectively, used in this study. Detectors of the same type were numbered for identification (IC1, IC2, IC3, FAR1, FAR2, FAR3, and FAR4). In the multi-dynamic and dynamic methods (Tables 2 and 3), each line was continued for the corresponding integration times (Int. t), and then were switched to the next sequence to complete a cycle; this process was repeated till the termination of measurements. In the static method, a cycle consisted of one line. A faraday cup (FAR4) or an ion counter (IC4) was employed depending on the expected intensity of $^{238}U^+$ signal intensity. In this study, isotopic measurements for 1 ng and 100 pg uranium utilized FAR4 detector because the $^{238}U^+$ signal intensities were expected to be above the working range of ion counters, whereas those for 30 pg, 5 pg, and 1 pg uranium and the individual particles used IC4 detector.

Detection efficiencies for the ion counters were adjusted using the ion signals of ^{187}Re (~300,000 cps). The mass bias for the isotopes was corrected by the isotopic measurement of a reference material (U200, National Bureau of Standards, USA).

The data sets, whose $^{238}U^+$ intensities were less than 5% of the maximum $^{238}U^+$ intensity, were discarded from data analysis to avoid unnecessary distortion of results arising from relatively small signal intensities. The other data sets were statistically processed as "valid data sets" in a measurement. To give greater weight to the data sets with higher intensities and vice versa, the weights (w_i) defined as follows were applied to all statistical calculations.

$$w_i = \frac{I_i^{238}}{\sum I_i^{238}} \tag{1}$$

where I_i^{238} is the signal intensity of $^{238}U^+$. The measurement uncertainty was estimated according to the guide to the expression of uncertainty in measurement (GUM) in accordance with the ISO/IEC Guide 98-3 [25,26].

All analyses were performed in a clean facility, which was controlled to ISO 5 and ISO 6 levels, to avoid any contamination of the samples, and complied with the quality control and quality assurance (QC/QA) system of the Korea Atomic Energy Research Institute (KAERI) [10,27].

3. Results and discussion

3.1. Experimental evaluation of three detection methods of TIMS using various amounts of U030 samples

Figs. 2, 3, 4, 5, and 6 summarize the results of the TIMS isotopic measurements of U030 samples with uranium amounts of 1 ng, 100 pg, 30 pg, 5 pg, and 1 pg, respectively. The drop line of each symbol represents the expanded uncertainty (U), which was calculated by multiplying coverage factor (k) with the combined standard uncertainty (u_c). The coverage factor was set to 2 at the confidence level of ~95%. The solid horizontal lines in each plot are the corresponding certified values. The scales of Figs. 2, 3, and 4 were manipulated to be the same for intuitive comparison, whereas Figs. 5 and 6 were adjusted to a different scale due to large uncertainties and broad dispersion. Averaged isotope ratio, averaged measurement uncertainty, accuracy of the averaged isotope ratio, and relative standard deviation (RSD) of isotope ratios of ten replicated measurements are summarized in Table 5. The measurement is more accurate when the accuracy is closer to zero. Negative accuracy